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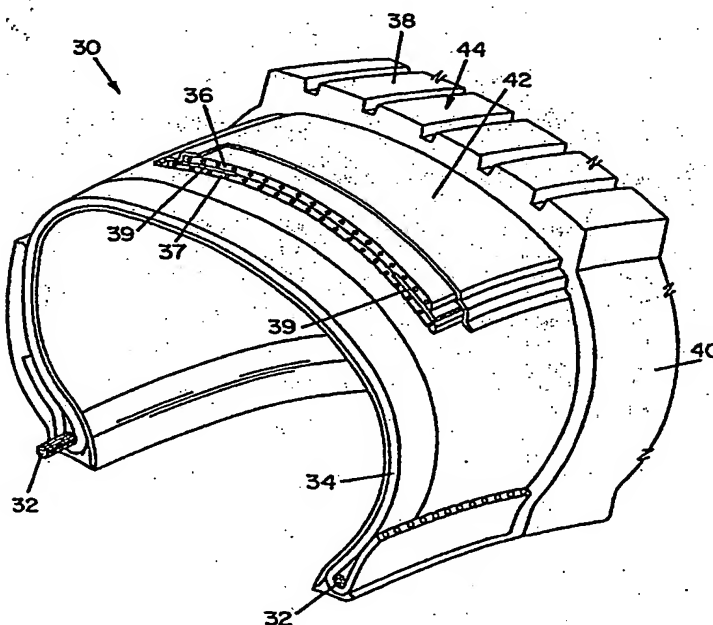
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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : B60C 1/00, 9/18, C08L 21/00</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 99/22951</b> (43) International Publication Date: 14 May 1999 (14.05.99)</p>
<p>(21) International Application Number: PCT/US97/19806 (22) International Filing Date: 30 October 1997 (30.10.97) (71) Applicant (for all designated States except US): THE GOODYEAR TIRE &amp; RUBBER COMPANY [US/US]; 1144 East Market Street, Akron, OH 44316-0001 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): PATITSAS, George, Philemon [US/US]; 660 Ada Street, Kent, OH 44240 (US); BRENNER, Jerry, Lawrence [US/US]; 284 Misty Lane, Copley, OH 44321 (US); SANDSTROM, Paul, Harry [US/US]; 96 Milton Drive, Tallmadge, OH 44278 (US); MIZNER, Eric, Charles [US/US]; 6075 Fox Chase Drive, Wadsworth, OH 44281 (US). (74) Agent: WHEELER, David, E.; The Goodyear Tire &amp; Rubber Company, Dept. 823, 1144 East Market Street, Akron, OH 44316-0001 (US).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  Published With international search report.</p>

(54) Title: TIRES HAVING IMPROVED HIGH SPEED PROPERTIES



(57) Abstract

A pneumatic tire which has belts, gum strips and an overlay which contains 2 to 15 phr thermoplastic reinforcing polymer as an addition to the compound, or as a replacement for 5 to 25 phr carbon black, has good high speed properties.

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## TIRES HAVING IMPROVED HIGH SPEED PROPERTIES

### 5 Background of the Invention

The invention relates to tires that have improved high speed properties.

Conventionally tires are loaded with high surface area carbon black to provide good tear strength and increase the modulus of the rubber. A high level of fine carbon black, however, causes the tires to have a high hysteresis, which contributes to a high rolling  
10 resistance, which works against high speed properties.

In the conception of the present invention, it was proposed that if the level of carbon black was reduced, and the omitted carbon black was replaced with a filler material that reduced the hysteresis of tire components in the crown area of the tire while maintaining stiffness, that rolling resistance could be improved, with a complementary improvement in  
15 high speed properties.

It is an object of the present invention to provide a tire with improved high speed properties.

Other objects of the invention will be apparent from the following description and claims.

### 20 Summary of the Invention

A pneumatic tire is provided comprising a pair of axially spaced apart annular beads, carcass plies wrapped around the beads, reinforcing belt plies disposed over the carcass plies in a crown area of the tire, gum strips disposed between edges of the belt, and an overlay disposed radially outward of the belts, tread disposed radially outward of the overlay, and  
25 sidewalls disposed between the tread and beads. The elastomer of the belts, overlay and gum strips comprises a polymer blend of 2-15 parts by weight thermoplastic reinforcing polymer per 100 parts by weight tread rubber (2-15 phr). In the illustrated embodiment, the polymer blend has a 100% modulus of 5.5 to 7.5.

The improved properties described herein are observed when the reinforcing polymer  
30 is mixed into the rubber used in the crown area reinforcement (the belts, gum strips and overlay) in a two step process where reinforcing polymer domains are predeveloped in a master batch as a first step in the process. Also, the improved tire properties described are observed only when the reinforcing domains are in all three components of the crown area reinforcement as described above.

35 In illustrated embodiments, the thermoplastic reinforcing polymer is polyamide or polypropylene, and the elastomer comprises polybutadiene, polyisoprene, styrene/butadiene

copolymers, and mixtures thereof. The thermoplastic reinforcing polymer may be grafted to the tread rubber using a grafting agent.

#### Brief Description of Drawings

Figure 1 illustrates a cross section of a tire delineating the tread base and tread cap.

5 Figure 2 illustrates a belt ply containing thermoplastic domains/fibers.

Figure 3 illustrates a gum strip with thermoplastic domains/fibers.

Figure 4 illustrates an overlay ply containing thermoplastic domains/fibers.

Figure 4a illustrates a spiral overlay containing thermoplastic domains/fibers.

#### Detailed Description of the Invention

10 With reference now to Fig. 1, a tire 30 of the invention is illustrated having a tread 44, and an overlay 42 and gumstrips 39, in addition to beads 32, sidewalls 40, carcass plies 34 and belts 36.

It has been found that the improved tire properties described herein are observed only when the reinforcing polymers are included in the elastomers of the crown reinforcement of  
15 the tire, i.e. the wire coat compound (elastomer of the belt plies), the elastomer in the gum strips and the elastomer in the overlay ply.

The crown reinforcement elastomers, in addition to conventional polymers, includes 2-30 phr thermoplastic resins. Such thermoplastic resins may be included as replacement for 5-25 phr carbon black in the elastomer.

20 Examples of thermoplastic resins that may be used in the elastomer include polyamides and polypropylene.

The filled elastomers, illustrated for use in the crown reinforcement, have a 100% modulus of 5.5 to 7.5. By contrast, the same rubber formulations, without thermoplastic resin reinforcement, and a reinforcing amount of carbon black, have a 100% modulus of about 3.5  
25 to 4.5.

Crown reinforcement elastomers made with the thermoplastic reinforcing polymer of the invention are prepared by a two step process. The first step involves the preparation of a polymer alloy containing thermoplastic reinforcing polymer. This process is described in U.S. patents 4,937,290 and 4,996,262, which are incorporated herein by reference. The second  
30 stage of the process is the blending of the polymer alloy of step one with polymers, such as rubbers, and other compounding ingredients, in conventional mixers, such as Banbury® mixers, extruders, or a mill mixer. The second step blending or mixing can be accomplished using compounding techniques well known in the art.

In the process of producing the alloy at elevated temperatures, a micro dispersion of the thermoplastic reinforcing polymer in an elastomer matrix is obtained. Such high temperatures cannot be achieved during normal Banbury mixing and such a micro dispersion cannot be obtained at normal temperatures, thus requiring the two-stage process.

5 The elastomers blended with the thermoplastic alloy in the second step of the process are preferably rubbers having carbon-carbon unsaturation, which can be sulfur cured. Examples of such rubbers are cis-1,4-polyisoprene (natural or synthetic), cis-1,4-polybutadiene, 3,4-polyisoprene, styrene/butadiene copolymers, styrene/isoprene/butadiene terpolymers, butadiene/acrylonitrile copolymers and isoprene/acrylonitrile copolymers, and  
10 mixtures thereof. Generally, a mixture of two or more of natural rubber and synthetic rubbers, such as cis-1,4- polyisoprene, cis-1,4-polybutadiene, 3,4-polyisoprene, styrene/butadiene copolymers and styrene/isoprene/butadiene terpolymers is preferred.

Those skilled in the art will recognize that small amounts of additional curatives (other than sulfur), such as peroxides, can be used in the composition.

15 Polybutadiene rubbers having low to high vinyl content, in the range of 30 to 90%, preferably 40 to 70%, can also be used.

The styrene/butadiene copolymer rubber (SBR) can be a solution type or an emulsion polymerization rubber with a wide range of vinyl content.

Various additives can be used and mixed with the rubber composition, such as carbon  
20 black, silica, rubber processing oils, sulfur cure accelerators and retarders, antidegradants, zinc oxide, zinc stearate and/or zinc acid, and other pigments, as desired.

If desired, a third step may be used in the mixing process wherein the sulfur and accelerators are withheld from the second step, and added separately in a third step.

Other such variations in the mixing of the elastomer compositions used in the invention  
25 will be apparent to those skilled in the art.

Lab testing suggests that physical properties of a wire coat compound (elastomer used to make reinforcing belts in a tire) are optimized for stiffness, wire adhesion, and high temperature durability when sufficient amounts of a nylon/natsyn blend (nylon 12 mixed with synthetic 2,4 polybutadiene) are used to replace an equal amount of carbon black with nylon  
30 12, for example 7.5 phr (7.5 parts by weight nylon 12 per hundred parts by weight rubber) in place of (i.p.o.) 7.5 phr carbon black, as in the example.

Thermoplastic reinforced elastomers may be used in any part of a tire where elastomers are used, but to enhance high speed properties, it is preferred that the alloys be used in the belt

properties was observed when the alloys of the invention were tested in the belts, only or the overlay and gum strips only.

As illustrated in the examples, the 100% modulus of elastomers that are filled with nylon 12 is increased substantially over the modulus of the same elastomer that is filled with carbon black as a reinforcing agent. Meanwhile, the rebound properties of the same elastomer filled with nylon 12 are similar to the properties of the carbon black filled elastomer. The invention is further illustrated with reference to the following examples.

#### EXAMPLE I

A nylon 12/polyisoprene alloy was produced in a Berstorff 43mm co-rotating twin screw extruder. The twin screw extruder was operated at 55 rpm (revolution per minute) to provide an extrudate temperature of about 230°C. The starting materials were introduced using loss-in-weight feeders and were introduced into the first barrel section. The overall feed rate of materials was 30 lbs./hr., wherein nylon 12 was added at a rate of 5.98 lbs./hr, polyisoprene was added at a rate of 23.8 lbs./hr, and 0.46 lbs./hr comprised a mixture of dithiodipropionic acid, thiodiphenylamine and an antioxidant.

The alloy thus produced was formulated into an elastomer having the following general composition used in the examples is shown in Table 1. The amounts of ingredients shown in this table, and throughout the specification, are in phr, unless otherwise indicated.

Table 1

1 <sup>st</sup> Non-Productive	
Natural Rubber	50.0
Synthetic cis-1,4-polyisoprene rubber <sup>(1)</sup>	50.0
Carbon Black <sup>(2)</sup>	Variable
Fatty Acid	2.0
Processing Oil <sup>(3)</sup>	1.0
Resorcinol	2.0
Zinc Oxide	5.0
Nylon/NAT2200	Variable
Productive	
Antidegradant <sup>(4)</sup>	.75
Zinc Oxide	3.0
Accelerators, Resin <sup>(5)</sup>	4.0
Sulfur	2.4
Retarder <sup>(6)</sup>	0.1

(1) NAT2200 from The Goodyear Tire & Rubber Company

(2) HAF type carbon black

(3) Naphthenic/Paraffinic oil

(4) amine type

(5) sulfenamide accelerators plus hexamethoxymethyl-melamine

(6) phthalimide type

#### EXAMPLE II

The rubber compositions containing the materials set out in Table 1 were prepared in a BR Banbury rubber mixer using two different stages of addition (mixing). A non-productive stage was mixed for about 4 minutes to a final temperature of about 160°C, and a final productive stage was mixed for about 2 minutes to a final temperature of about 110°C. The cure behavior and cured properties of the compounds are shown in Table 2.

The physical properties characterizing the compounds in the table are well known to those skilled in the art.



Compounds 1, 3, and 4 were selected for evaluation in a tire program. Compound 4 is used as the control.

In the table the amount of nylon/nat2200 blend used in the composition in phr is described, followed in parentheses by the overall amount of nylon used in the composition in phr, for example, 37.5(7.5).

Also, dNm represents deci Newton meters, and MPa represents megapascals.

Table 2

Sample #	1	2	3	4	5	6	7	8	9
Carbon	52.5	45	60	60	60	45	52.5	45	52.5
Black phr									
Nylon/	37.5	0	37.5	0	75	75	0	75	75
NAT2200 phr	(7.5)		(7.5)		(15)	(15)		(15)	(15)
<u>Rheometer,</u>									
<u>150°C</u>									
Max	61.4	49.8	65.9	61.7	72.6	65.2	54.5	53.6	68.1
Torque, dNm									
Min	9.5	7.2	10.5	10.2	14.2	11.2	8.4	7.4	11.9
Torque, dNm									
Delta	51.9	42.6	55.4	51.5	58.4	54.0	46.1	46.2	56.2
Torque, dNm									
T90,	20.5	18.4	21.6	20.0	22.1	21.3	19.9	19.9	20.9
Minutes									
<u>Stress-Strain</u>									
Tensile	20.5	23.5	19.5	22.5	17.8	17.2	19.2	16.9	15.2
Strength, Mpa									
Elongation	465	560	430	440	330	398	531	460	356
At Break, %									
100% Modulus,	4.8	2.2	5.2	3.2	6.6	6.0	3.0	4.0	6.0
Mpa									
<u>Rebound</u>									
100°C, %	54	57	51	52	47	55	57	59	53
<u>Hardness</u>									
100°C	78	67	80	75	83	75	70	69	77

The value in parantheses represents Nylon phr in the final rubber composition.

Compounds 10, 11 and 12 were prepared in a factory Banbury mixer to be used in the tire program illustrated in Example III. Compound 11 was selected to evaluate the affects of higher hardness and modulus as compared to the control in a compound having rebound similar to the control, whereas compound 12 was selected for evaluation of a compound with

higher rebound as compared to the control and hardness similar to that of the control. Compound 10 is the comparison or control compound.

Table 3

Sample #	10	11	12
Carbon Black	60	60	52.5
Nylon/NAT2200	0	37.5 (7.5)	37.5 (7.5)
<b>Rheometer (150°C)</b>			
Max. Torque, dNm	58.1	64.6	60.0
Min. torque, dNm	11.6	12.0	11.1
Delta torque, dNm	46.5	52.6	48.9
T90, minutes	18.3	20.3	19.3
<b>Stress-Strain</b>			
Tensile Strength, Mpa	20.0	19.2	6
Elongation at Break, %	427	331	368
100% Modulus, MPa	4.0	6.6	5.7
300% Modulus, MPa	14.9	19.1	17.5
<b>Rebound</b>			
100°C, %	56	56	60
<b>Hardness</b>			
100°C	76	79	75
<b>Rheovibron</b>			
E' at 60°C, Mpa	13.0	62.0	44.0
Tan Delta at 60°C	.064	.074	.068

### Example III

The control compound (Sample #10) and the experimental compounds (Samples #11 and #12 from Table 3) were evaluated in P225/50VR16 Eagle passenger tires. The experimental compounds were evaluated in the wirecoat, gum strips and overlay. The description of the constructions evaluated are shown in Table 4. All constructions (1-5) exhibited similar handling, rolling resistance and durability. The use of Sample #11 (construction 2) in all components as shown in Table 4 gave significantly better high speed results in the laboratory step test (where the speed on a test machine is increased in increments until the tire fails). Two tires of each construction were tested.

Apparently the combination of higher hardness and similar rebound in all three tire components (construction 2) gave improved high speed performance over the control construction. Construction 3, prepared using compounds with higher rebound and similar

hardness, as compared to the control, did not show improvement over the control (construction 1).

Table 4

Construction	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
Wire Coat	Cont	Sample #11	Sample #12	Cont	Cont
Gum Strip	Cont	Sample #11	Sample #12	Sample #12	Cont
Overlay	Cont	Sample #11	Sample #12	Cont	Sample #12
Speed steps	-	+	-	-1/2	-1

In the table, the dash (-) indicates the performance of the control tire in the speed step test, + indicates an improvement of one speed step over the control, and the minuses indicate performance levels less than the control.

While specific embodiments of the invention have been illustrated and described, those skilled in the art will recognize that the invention may be variously modified and practiced without departing from the spirit of the invention. The invention is limited only by the scope of the following claims.

## CLAIMS

1. A pneumatic tire comprising a pair of axially spaced annular beads, carcass plies wrapped around said beads, reinforcing belts disposed over said carcass plies in a crown area of said tire and gum strips associated with belt edges, tread disposed over said belts in said crown area, and an overlay interposed between said tread and said belts, and sidewalls  
5 disposed between said tread and said beads, wherein elastomers used in said belts, gum strips and overlay comprise 2-30 phr thermoplastic polymer in rubber, said elastomer having a 100% modulus of 5.5 to 7.5.
2. The tire of claim 1 in which said thermoplastic polymer is polyamide or polypropylene  
10 and said elastomer is selected from the group consisting of cis-1,4-polyisoprene (natural or synthetic), cis-1,4-polybutadiene, 3,4-polyisoprene, styrene/butadiene copolymers, styrene/isoprene/butadiene terpolymers, butadiene/acrylonitrile copolymers, isoprene/acrylonitrile copolymers, and mixtures thereof.
3. The tire of claim 1 in which said thermoplastic polymer is polyamide and said  
15 elastomer is natural rubber and SBR.
4. The tire of claim 1 in which said thermoplastic polymer is polypropylene.
5. The tire of claim 1 wherein the elastomer used in the overlay, gumstrips and wire coat  
is made by mixing 5 to 80 phr thermoplastic resin with rubber in a co-rotating twin screw  
extruder to form a resin/elastomer alloy, and the alloy thus produced was formulated into an  
20 elastomer to yield a final concentration of 2 to 30 phr thermoplastic resin in said elastomer.

6. The tire of claim 5 wherein the elastomer of the gumstrips, overlay and wire coat comprises in a non-productive composition comprising

Natural Rubber	50.0 phr
Synthetic cis-1,4-polyisoprene rubber	50.0 phr
Carbon Black	45-60 phr
Fatty Acid	2.0 phr
Processing Oil	1.0 phr
Resorcinol	2.0 phr
Zinc Oxide	5.0 phr
Nylon/NAT2200	37.5 to 75 phr

and a productive composition comprising

Antidegradant	.75 phr
Zinc Oxide	3.0 phr
Accelerators, Resin	4.0 phr
Sulfur	2.4 phr
Retarder	0.1 phr

7. The tire of claim 6 wherein the said alloy was produced in a twin screw extruder which was operated at 55 rpm (revolution per minute) to provide an extrudate temperature of about 230°C, and wherein the starting materials were introduced using loss-in-weight feeders in the first barrel section, wherein the overall feed rate of materials was 30 lbs./hr. and thermoplastic resin was added at a rate of 5.98 lbs./hr and elastomer was added at a rate of 23.8 lbs./hr, and a mixture of dithiodipropionic acid, thiodiphenylamine and an antioxidant were added at a rate of 0.46 lbs./hr.

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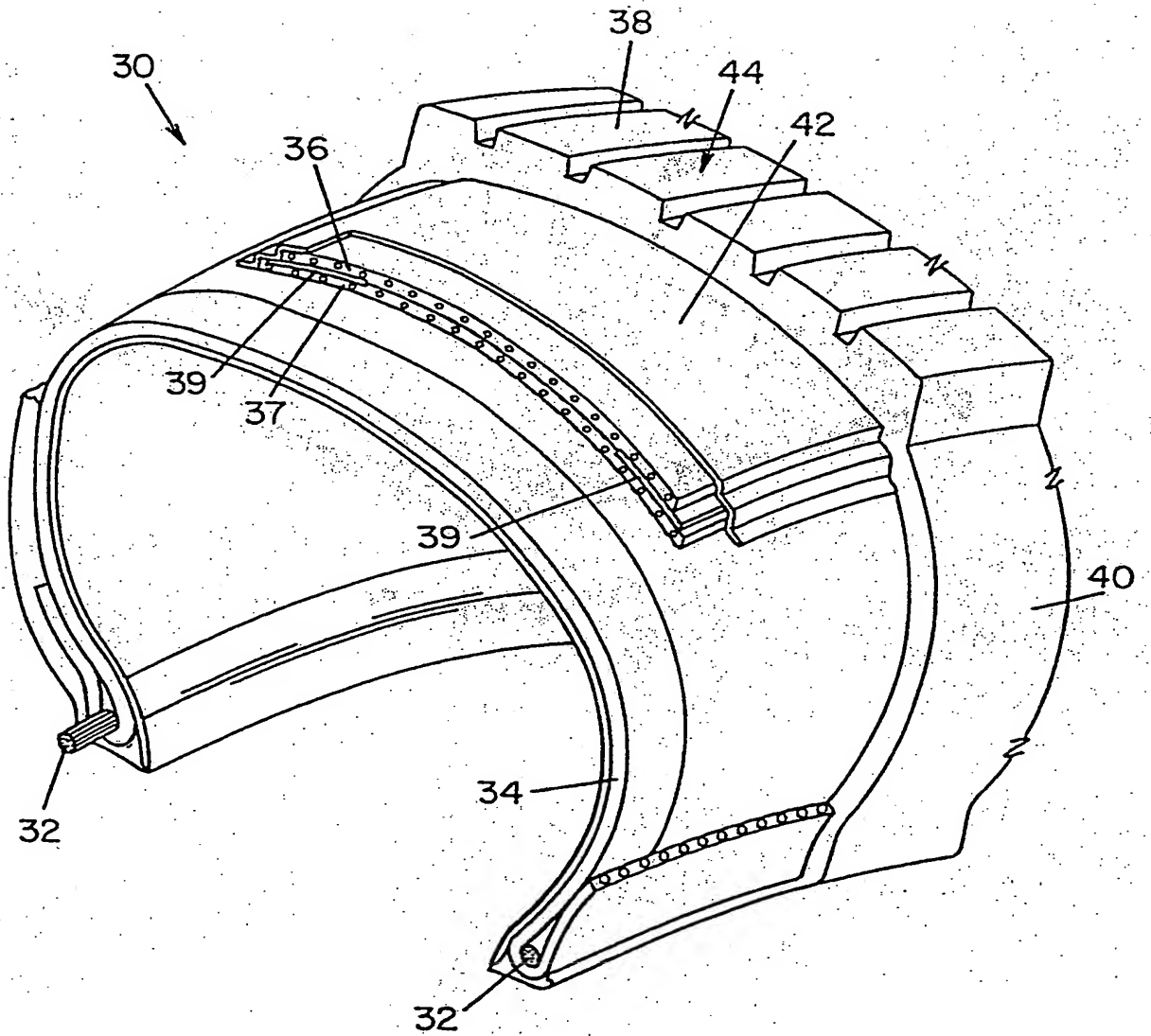


FIG. 1

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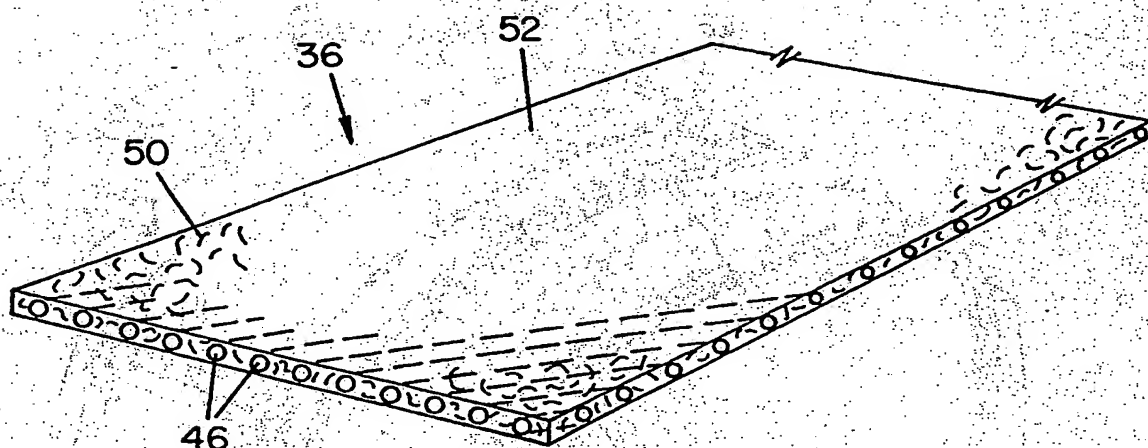


FIG. 2

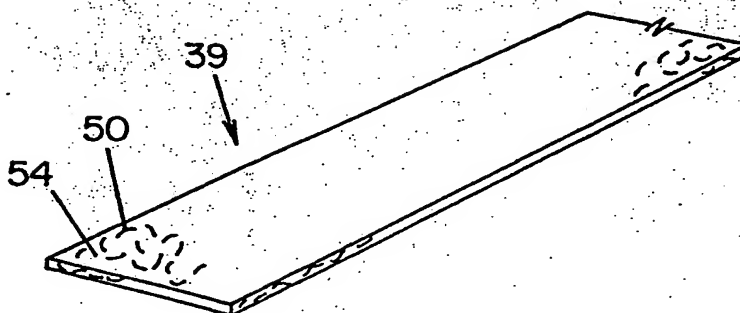


FIG. 3

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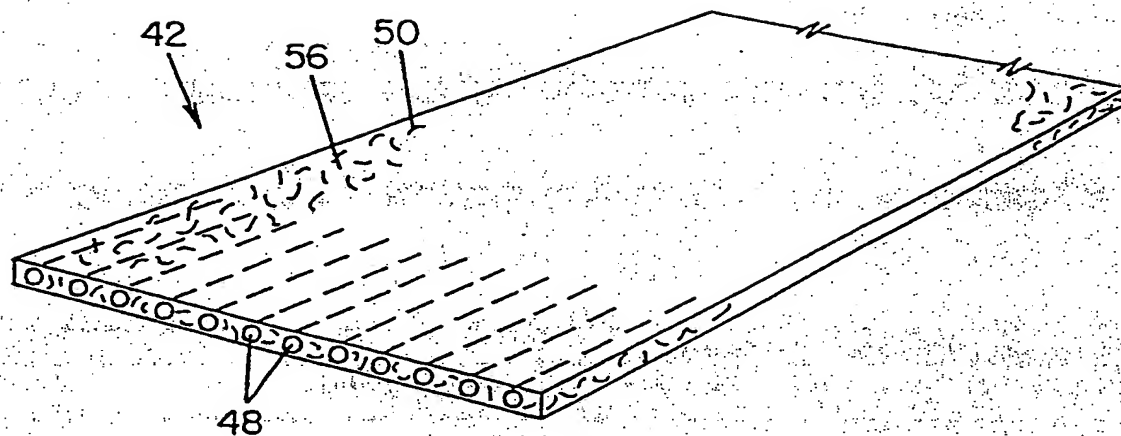


FIG. 4

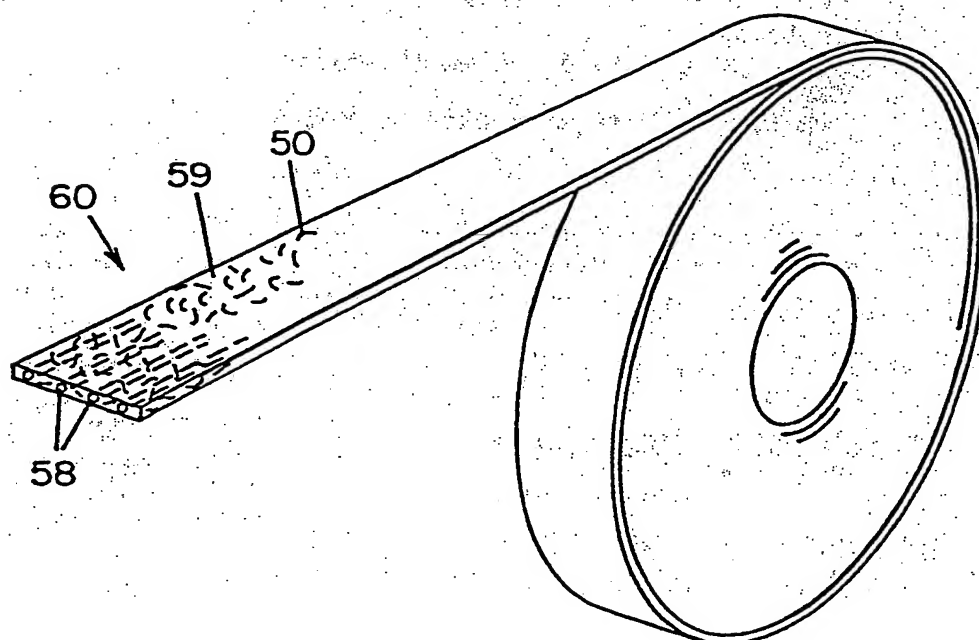


FIG. 4A



# INTERNATIONAL SEARCH REPORT

Int. J. Application No.  
PCT/US 97/19806

**A. CLASSIFICATION OF SUBJECT MATTER**  
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**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 049 610 A (TAKAKI TAKESHI ET AL) 17 September 1991 see claims; examples; tables	1-7
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A	EP 0 645 431 A (GOODYEAR TIRE & RUBBER) 29 March 1995	1
A	EP 0 445 486 A (GOODYEAR TIRE & RUBBER) 11 September 1991 see page 4, line 5 - line 10; claims; table 1 see page 4, line 50 - page 5, line 47 -/-	1,2,4,5,7

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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 645 263 A (GOODYEAR TIRE & RUBBER) 29 March 1995 see claims; tables	1-7
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A	US 3 916 968 A (MASSON YVES) 4 November 1975 see column 1, paragraph 1 - paragraph 2; examples	1

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Information on patent family members

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